

L/L Equilibria of Dimethylcyclopropanecarboxylic Acid in Water—Solvent Systems with Trioctylamine as an Extractant*

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L/L equilibrium data for (*R*)-2,2-dimethylcyclopropanecarboxylic acid (DMCCA) in the system water—organic solvent are presented together with the corresponding chemism and the related extraction model. Pure saturated acyclic unbranched alkanes and their mixture with trioctylamine (TOA) as an extractant were used as solvents. A high loading of amine extractant, achieving the value of about 27, was observed. The loading was independent of the extractant concentration, especially at concentrations of DMCCA in the aqueous phase (c_F^*) lower than 0.12 kmol m^{-3} . This suggests the (*p*,1) stoichiometry of complexes where *p* is the number of acid molecules per one molecule of extractant in the complex. In pure alkanes, DMCCA is supposed to be present in the form of a monomer and a dimer, but the possibility of formation of a trimer at higher concentrations should be examined. The equilibrium data for the reactive extraction were correlated using the model equations considering up to 14 molecules of DMCCA per one molecule of TOA. A reduction of 14 complexes involved to 5 was found possible including (1,1), (3,1), (4,1), (6,1), and (10,1) types together with a monomer and a dimer of acid. A good fit of the model to the experimental data was achieved.

Isolation or recovery of organic acids from fermentation broths or waste solutions can be performed by solvent extraction [1–4] or pertraction through liquid membranes [5–8].

The *R*-isomer of 2,2-dimethylcyclopropanecarboxylic acid (DMCCA) is a by-product of the enzymatic resolution of the racemic mixture of DMCCA esters. The waste solution contains the *R*-isomer of DMCCA in the form of a sodium salt (pH 8). At pH of about 2, pure DMCCA forms a separate organic phase, due to a lower solubility of undissociated DMCCA of about 19 g dm^{-3} . The rest of DMCCA remains dissolved in the aqueous phase and has to be separated by another method.

The extraction of carboxylic and hydroxycarboxylic acids from aqueous solutions by higher tertiary amines such as trioctylamine (TOA) was studied in papers [2, 9–15]. Important works on the extraction of carboxylic acids by amine extractants were published by *Tamada et al.* [16–18]. Overloading of the solvent with amine extractants, *i.e.* formation of complexes with more than one acid molecule per one amine molecule, was observed [16, 17, 19]. *Juang and Huang* [20, 21] studied the extraction of citric and lactic acids by TOA in detail and presented a mathe-

tical model. The influence of various diluents on the extraction of formic, levulinic, and acetic acids by Alamine 336 was studied by *Senol* [22]. No equilibrium data on the extraction of DMCCA by organic solvents are available in the literature. The experimental results on pertraction of DMCCA in HF contactors were presented in [23, 24]. Data on the extraction of the structurally similar butyric acid were published in [25], where the extraction efficiency of 14 solvents was tested. The highest distribution ratios have been achieved for solvents containing tertiary amine. *Sabolová et al.* [19, 26] reported equilibrium data and the model of extraction of butyric acid for alkanes and solvents containing TOA. The extraction equilibria of acids in the system water—organic solvent are important in modelling mass transfer through liquid membranes and in hollow fibre contactors.

The aim of this work was to measure and model the L/L extraction equilibria of DMCCA for solvents containing TOA in an aliphatic diluent.

THEORETICAL

In modelling the extraction equilibria of organic acids in the system water—solvent containing TOA

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following assumptions were considered:

i) Two interactions of the acid with the organic solvent:

a) physical dissolving of the acid in a solvent or diluent in the form of a monomer, dimer, and trimer of acid;

b) chemical reaction of the acid with an extractant (TOA) and formation of complexes with different structure.

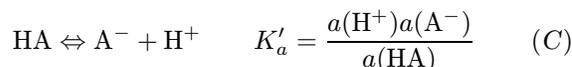
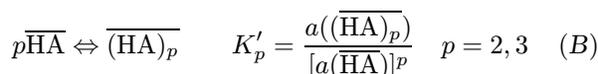
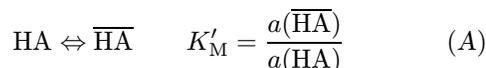
ii) Neither extractant, nor complexes are soluble in the aqueous phase.

iii) The volumes of the phases depend on the acid concentration in the given phase. Additivity of the volumes of the solvent and the acid has been confirmed experimentally.

iv) Hydration of complexes is not considered in the model.

Physical Extraction

For the extraction of a carboxylic acid to nonpolar organic solvents, *e.g.* to alkanes the following reaction scheme is proposed



where K'_M is the extraction constant of the monomer and K'_p is the thermodynamic equilibrium constant of the formation of associates of the physically extracted acid in the solvent from a monomer containing p molecules of the acid (dimer and trimer). The terms $a(\text{X})$ denote the activity of species shown and the overbar denotes species in the organic phase. The apparent extraction constant of a monomer and the equilibrium constants of formation of acid associates, based on molar concentrations, are defined by the equations

$$K_M = \frac{[\overline{\text{HA}}]}{[\text{HA}]} = \frac{c_M}{c_F^*} \quad (1)$$

$$K_p = \frac{[\overline{(\text{HA})}_p]}{[\text{HA}]^p} = \frac{c_p}{(c_M)^p} \quad p = 2, 3 \quad (2)$$

$$K_a = \frac{[\text{A}^-][\text{H}^+]}{[\text{HA}]} \quad (3)$$

where c_M is the concentration of the monomer in the solvent, c_p is the concentration of the associate of p molecules of the carboxylic acid (dimer or trimer) and c_F^* is the equilibrium concentration of the undissociated acid in the aqueous phase, which can be estimated from the equation

$$c_F^* = \frac{c_{\text{aF}}^*}{1 + 10^{(\text{pH}_F^* - \text{p}K_a)}} \quad (4)$$

where c_{aF}^* is the total (analytical) concentration of the acid in the equilibrium aqueous phase. Dissociation constants or $\text{p}K_a$ of aliphatic carboxylic acids are very similar, *i.e.* values of $\text{p}K_a$ at 25 °C for propionic, butyric, and pentanoic acids are 4.87, 4.82, and 4.81, respectively [27]. For DMCCA the value of $\text{p}K_a = 4.82$ was used in this work.

The overall concentration of the acid in alkanes or in another solvent without reactive extractant is according to the material balance and eqn (2) as follows

$$c_{\text{aS}} = c_M + \sum_p c_p = K_M c_F^* + \sum_p (pK_p (K_M c_F^*)^p) \quad (5)$$

The distribution ratio of the acid is defined by the relation

$$D = \frac{c_{\text{aS}}}{c_F^*} \quad (6)$$

or $p = 2$, from eqns (2), (5), and (6) it follows

$$D = K_M + 2K_2(K_M)^2 c_F^* \quad (7)$$

which means that the distribution coefficient is a linear function of the acid concentration in the aqueous phase. When also an acid trimer formation in pure alkanes is considered, the equation for the distribution coefficient, equivalent to eqn (7), will be a quadratic one, so the concentration dependence of the distribution coefficient will be nonlinear.

Reactive Extraction of the Acid by an Extractant

Taking into account assumption i), both physical dissolving of DMCCA and formation of the acid complex with extractant are supposed. Further it is assumed that for the distribution of the acid in alkanes equilibrium constants found for pure alkanes can be applied.

For the volume of alkanes and the physically extracted organic acid the equation

$$\begin{aligned} V_{\text{Sphys}} &= V_{\text{alk}} + V_{\text{Aphys}} = \\ &= V_{\text{So}} \left(1 - \frac{c_{\text{Po}} M_{\text{P}}}{\rho_{\text{P}}} \right) + \frac{n_{\text{Sphys}} M_{\text{A}}}{\rho_{\text{A}}} \end{aligned} \quad (8)$$

can be derived, where c_{Po} is the initial concentration of extractant in the pure solvent and the term in brackets represents correction for a volume of extractant. The molar amount of the physically extracted acid in the solvent is

$$\begin{aligned} n_{\text{Sphys}} &= \left[K_M c_F^* + \sum_p (pK_p (K_M c_F^*)^p) \right] V_{\text{Sphys}} = \\ &= \frac{Y V_{\text{So}} \left(1 - \frac{c_{\text{Po}} M_{\text{P}}}{\rho_{\text{P}}} \right)}{1 - Y \frac{M_{\text{A}}}{\rho_{\text{A}}}} \end{aligned} \quad (9)$$

where

$$Y = K_M c_F^* + \sum_p (p K_p (K_M c_F^*)^p) \quad (10)$$

For the ratio of volumes of the pure solvent and the solvent with the extracted acid in all forms (physical and reactive extraction) the equation can be derived

$$\frac{V_{S0}}{V_S} = 1 - \frac{c_{aS}^* M_A}{\rho_A} \quad (11)$$

where c_{aS}^* is the total equilibrium concentration of the acid in the solvent. Combining eqns (9) and (11) for the concentration of the physically extracted acid the following relationship

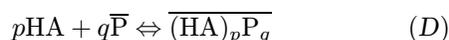
$$\begin{aligned} c_{aSphys}^* &= \frac{n_{aSphys}}{V_S} = \\ &= \left(1 - \frac{c_{aS}^* M_A}{\rho_A}\right) \left(1 - \frac{c_{Po} M_P}{\rho_P}\right) \frac{Y}{1 - Y \frac{M_A}{\rho_A}} \quad (12) \end{aligned}$$

can be derived.

In the case of amines, the affinity of the extracted acid HA to the extractant P is of the acid-base nature. The organic phase is mostly able to dissolve a larger amount of acid than it corresponds to the mole ratio acid:extractant = 1:1 [13, 16, 17, 19, 26]. The loading of the extractant, z , is defined as the ratio of the overall acid concentration in the organic phase in the form of complexes with the extractant P and the overall (analytical) amine concentration in the organic phase [16]

$$z = \frac{c_{aS}^* - c_{aSphys}^*}{c_{app}} \quad (13)$$

Formation of the acid/extractant complexes can be expressed by the overall reaction



where P means the reactive extractant. For the monocarboxylic acids it is characteristic that they form complexes containing one or more acid molecules with one molecule of amine in the complex, as shown in papers [17, 19]. Instead of the general stoichiometry of the complexes (p, q) stoichiometry ($p, 1$) with corresponding thermodynamic equilibrium (extraction) constants defined as

$$K'_{p,1} = \frac{a(\overline{(\text{HA})_p \text{P}})}{(a(\text{HA}))^p a(\bar{\text{P}})} \quad (14)$$

can be supposed. The apparent equilibrium constants of formation of the ($p, 1$) complexes, based on the molar concentrations, are defined by the equation

$$K_{p,1} = \frac{[\overline{(\text{HA})_p \text{P}}]}{[\text{HA}]^p [\text{P}]} = \frac{c_{p,1}}{(c_F^*)^p c_P} \quad (15)$$

where $c_{p,1}$ is the concentration of the given ($p, 1$) complex containing p molecules of HA and one molecule

of extractant P and c_P is the concentration of the free extractant in the solvent.

The overall analytical (total) concentration of the extractant P in the organic phase is

$$c_{aP} = c_{Po} \left(1 - \frac{c_{aS}^* M_A}{\rho_A}\right) \quad (16)$$

where the term in the brackets is the correction for the change of the extractant concentration due to the change in the volume of the solvent phase connected with extraction of the acid. For the concentration of the free (uncomplexed) extractant in the solvent it can be written

$$c_P = c_{aP} - \sum_p c_{p,1} \quad (17)$$

By substitution for the concentrations of individual complexes into this equation and from eqn (15) one gets

$$c_P = c_{aP} - c_P \sum_p (K_{p,1} (c_F^*)^p) \quad (18)$$

and after rearrangement it follows for the concentration of the free extractant

$$c_P = \frac{c_{aP}}{1 + X} \quad (19)$$

where

$$X = \sum_p (K_{p,1} (c_F^*)^p) \quad (20)$$

The analytical (overall) concentration of the acid extracted by extractant P is given as the sum of the concentrations of ($p, 1$) complexes, according to eqns (15) and (18), multiplied by p

$$c_{aSreact} = c_P \sum_p (p K_{p,1} (c_F^*)^p) = \frac{c_{aP}}{1 + X} B \quad (21)$$

where

$$B = \sum_p (p K_{p,1} (c_F^*)^p) \quad (22)$$

By combining eqns (12), (16), and (21) a relation for the overall equilibrium concentration of the acid in the solvent is obtained

$$c_{aS}^* = c_{aSphys}^* + c_{aSreact}^* = \frac{N}{1 + N \frac{M_A}{\rho_A}} \quad (23)$$

where

$$N = \left(1 - \frac{c_{Po} M_P}{\rho_P}\right) \frac{Y}{1 - Y \frac{M_A}{\rho_A}} + \frac{B c_{Po}}{1 + X} \quad (24)$$

Then for the distribution coefficient defined by eqn (6) it follows

$$D = \frac{N}{\left(1 + N \frac{M_A}{\rho_A}\right) c_F^*} \quad (25)$$

The interaction of DMCCA with free TOA is assumed to be a rapid acid-base reaction resulting in the formation of the (1,1) complex. Furthermore it was supposed that higher complexes with more DMCCA molecules per one TOA molecule are formed by hydrogen bonds between the OH group of the acid and the carboxylate group in the complex [17]. For example, when a chemism with a monomer and a dimer (1,0), (2,0) of acid and complexes (1,1), (3,1), (4,1), (6,1), and (10,1) is considered (as will be shown later), the following relations can be derived

$$B = K_{1,1}c_F^* + 3K_{3,1}(c_F^*)^3 + 4K_{4,1}(c_F^*)^4 + 6K_{6,1}(c_F^*)^6 + 10K_{10,1}(c_F^*)^{10} \quad (26)$$

$$X = K_{1,1}c_F^* + K_{3,1}(c_F^*)^3 + K_{4,1}(c_F^*)^4 + K_{6,1}(c_F^*)^6 + K_{10,1}(c_F^*)^{10} \quad (27)$$

Eqns (24) to (27) together with eqns (1) and (2) enable the description of L/L equilibria in the reactive extraction of DMCCA.

The mole fraction of acid in individual complexes of DMCCA and TOA with the (p,1) structure to the total content of acid in the solvent is defined by the relation

$$y_{p,1} = pc_{p,1}/c_S^* \quad (28)$$

and the mole fraction of the monomer, dimer and/or trimer ($p = 2$ or 3) in pure alkanes is given by the relations

$$y_M = c_M/c_S^* \quad (29)$$

$$y_p = pc_p/c_S^* \quad (30)$$

EXPERIMENTAL

Alkanes. The dodecane fraction of linear alkanes (Slovnaft Bratislava, SK) was used as a diluent. The composition estimated by GC (w_i /mass %), was 7.18 C₁₀, 32.39 C₁₁, 33.11 C₁₂, 36.84 C₁₃, and 0.28 C₁₄ and higher. The mean relative molecular mass was 166.95.

Trioctylamine (Fluka, Switzerland) with purity higher than 99 mass % was used as received.

(R)-2,2-dimethylcyclopropanecarboxylic acid (DMCCA, Lachema, Czech Republic), a liquid with purity higher than 99 mass % and with the relative molecular mass of 114.14. The solubility of DMCCA in water is about 19 kg m⁻³ (0.166 kmol m⁻³).

The properties of chemicals and solvents used are presented in Table 1.

20 cm³ of aqueous solution of DMCCA was contacted with 20 cm³ of solvent using a rotational shaking water bath in 500 cm³ Erlenmeyer flasks at a frequency of 180 min⁻¹ for 5 h at a temperature of (25 ± 0.1)°C. Due to the low solubility of DMCCA in water (about 19 g dm⁻³) a certain amount of pure DMCCA was added into the solvent to achieve higher equilibrium concentrations c_F^* . After separation of the

Table 1. Characteristics of Used Chemicals and Solvents at 25 °C

Chemical or solvent	ρ	$\nu \cdot 10^6$
	kg m ⁻³	m ² s ⁻¹
DMCCA	988.08	
Alkanes	743.1	1.730
0.2 kmol m ⁻³ TOA in alkanes	748.6	1.947
0.4 kmol m ⁻³ TOA in alkanes	754.3	2.207
0.6 kmol m ⁻³ TOA in alkanes	760.1	2.512

phases, the equilibrium pH of the aqueous phase was measured and the content of acid was analyzed.

The concentration of DMCCA in aqueous phases was determined isotachophoretically using an analyzer EA 100 (Villa, Slovakia). The concentration of DMCCA in organic phases was estimated also isotachophoretically after stripping the acid to the solution of NaOH.

The volumes of both phases in equilibrium were calculated according to the following expressions, when the additivity of volumes was assumed

$$V_F = \frac{V_{Fo}(\rho_A - c_{aFo}M_A)}{\rho_A - c_{aFo}^*M_A} \quad (31)$$

$$V_S = V_{So} + V_{Ao} + V_{Fo} - V_F \quad (32)$$

where V_{Ao} is the volume of acid (DMCCA) added directly to the solvent phase to achieve higher equilibrium concentrations in the aqueous phase close to the solubility of DMCCA (0.166 kmol m⁻³). In each experiment the mass balance of the acid was checked by the ratio

$$\varphi = \frac{c_F^*V_F + c_{aS}^*V_S}{m_A/M_A + c_{Fo}V_{Fo}} \quad (33)$$

In the ideal case, the value of φ should be 1. In the most measurements the mass balance ratio was within ± 3 % of this value.

The water content in the organic phases was determined by Karl Fischer titration with the reagent Hydranal-Composites (Merck, Germany) using the autotitrator DL 50 (Mettler Toledo, Switzerland).

RESULTS AND DISCUSSION

As a diluent for TOA alkanes were chosen because of their low toxicity to biomass in comparison with aromatics. Alkanes dissolve the complexes of DMCCA with TOA well without the requirement of a modifier, as it is the case of hydroxycarboxylic acids [7, 10, 14]. This could be important in the on-line extraction of organic acids from the fermentation broths, which enables to take the product away and to prevent its inhibition effect [2, 15]. Higher alcohols used as modifiers for the extraction of acids can be quite toxic to biomass [28].

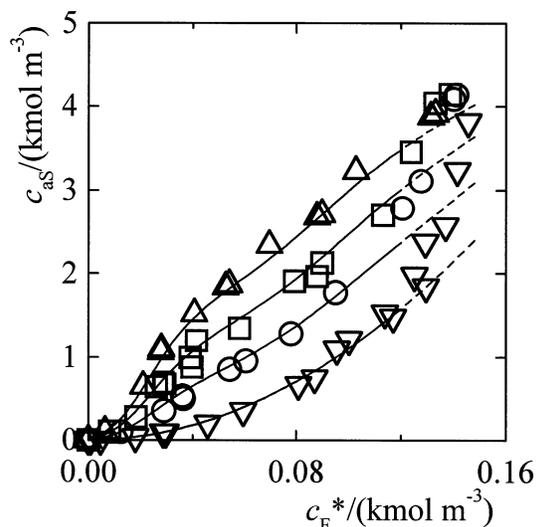


Fig. 1. Equilibrium concentration of DMCCA in the solvents *vs.* equilibrium concentration of acid in the aqueous phase. Lines represent the correlation of experimental data with eqns (5 and 23) considering mechanism I R or A I and taking into account data with the concentration of acid in the aqueous phase below 0.12 kmol m^{-3} . Solvents: ∇ alkanes; \circ 0.2 kmol m^{-3} , \square 0.4 kmol m^{-3} , \triangle 0.6 kmol m^{-3} TOA in alkanes.

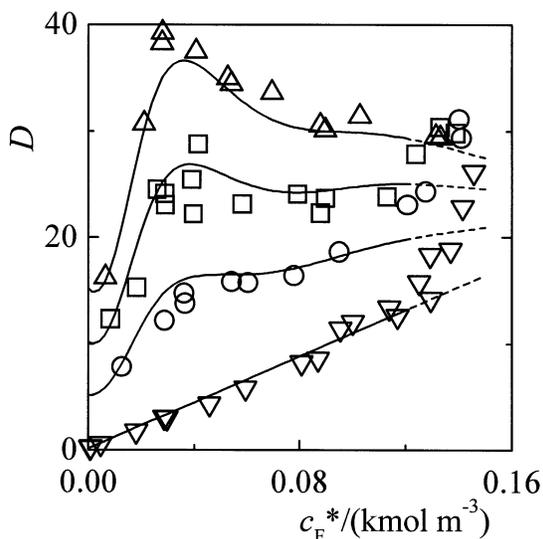


Fig. 2. Distribution ratio of DMCCA in water/solvent systems *vs.* concentration of DMCCA in the aqueous phase. Lines represent the correlation of experimental data with eqns (5 and 25) considering mechanism I R or A I and taking into account data with the concentration of acid in the aqueous phase below 0.12 kmol m^{-3} . The legend is the same as in Fig. 1.

Equilibrium data of DMCCA in the system water—solvent, presented in Figs. 1 and 2, show that also pure alkanes extract DMCCA significantly.

Table 2. Extraction Constant of the Monomer and Equilibrium Constants of Dimerization and Trimerization of DMCCA in Pure Alkanes

Equilibrium constants (kmol m^{-3}) ^{1-p}	Mechanism	
	A I	A II
K_M	0.1547	0.1547
K_2	2265	1729
K_3		2.397×10^4
r	0.9947	0.9967
SSD	5.898	3.596
σ	0.4590	0.3650

L/L Equilibria for Pure Alkanes

With increasing the concentration of DMCCA in the aqueous phase the value of the distribution coefficient of DMCCA in pure alkanes increases more or less linearly up to about 0.12 kmol m^{-3} . Above this concentration the distribution coefficient starts to increase more sharply, as shown in Fig. 2. The formation of higher associates, as discussed below, eqn (7), as well as the nonideal behaviour with activity coefficients differing from unity, or both, can explain the presented data.

Equilibrium data of DMCCA in the system water—pure alkanes were correlated by eqns (5) to (7). The results are summarized in Table 2 and presented together with the measured values in Figs. 1 and 2 where the lines are calculated according to the mechanism A I for data with the concentration of acid in the aqueous phase below 0.12 kmol m^{-3} . According to this mechanism, only the acid monomer and dimer are considered, as it was shown in the theoretical part. At higher concentrations in the aqueous phase the solubility of DMCCA in water is approached, that is about 19 kg m^{-3} ($0.166 \text{ kmol m}^{-3}$). The constants presented in Table 2 and data in Figs. 1 and 2 show that there is a strong physical extraction of DMCCA to alkanes connected with the lipophilic character of DMCCA, which is manifested by its limited water solubility. For the estimation of the extraction constant of the monomer, K_M , only data at low aqueous-phase concentrations, up to 0.05 kmol m^{-3} , were considered using the linear regression. According to eqn (7), K_M was determined as an intercept on the y -axis with the value of 0.1547, which was fixed for all further correlations. This value is higher than that of butyric acid presented by *Sabolová and Schlosser* [26], where $K_M = 0.0902$. The estimated dimerization constant for DMCCA $K_2 = 2155 \text{ m}^3 \text{ kmol}^{-1}$ is higher compared to the related dimerization constants of other carboxylic acids. *Juang and Wu* [29] determined the value of K_2 for acetic acid in xylene as $235.0 \text{ m}^3 \text{ kmol}^{-1}$, *Davies et al.* [30] for propionic acid in light petroleum calculated

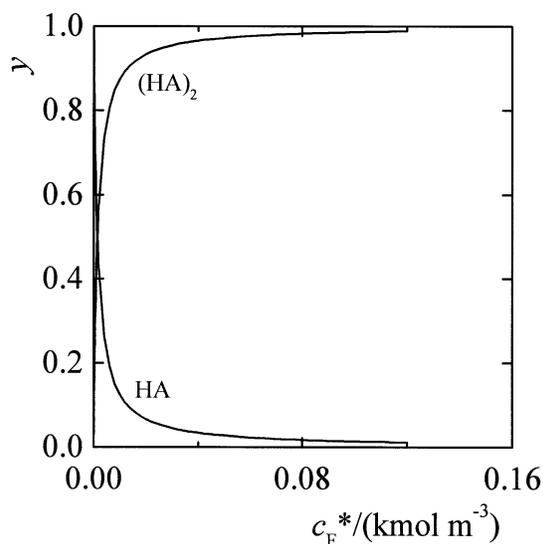


Fig. 3. Mole fraction of the individual forms of DMCCA in pure alkanes vs. equilibrium concentration of acid in the aqueous phase. Calculated using eqns (29, 30) considering mechanism A I.

$K_2 = 79.8 \text{ m}^3 \text{ kmol}^{-1}$, Sabolová and Schlosser [26] for butyric acid in alkanes $K_2 = 64.16 \text{ m}^3 \text{ kmol}^{-1}$ and Luque *et al.* [13] estimated this constant for valeric acid in toluene as $K_2 = 15.4 \text{ m}^3 \text{ kmol}^{-1}$. The distribution of a monomer and a dimer in the solvent in terms of their molar fractions, according to eqns (29) and (30) is shown in Fig. 3. At low concentrations, the most part of DMCCA in the solvent is in the form of the monomer, but very soon the dimer becomes to be a dominant form.

In the mechanism A II, presented in Table 2, also the formation of a trimer is considered and characterized by the equilibrium constant K_3 . This mechanism correlates the experimental data with a better fit as documented by lower values of SSD and standard deviation listed in Table 2. The existence of the trimer of DMCCA has to be proved by chemical analysis.

L/L Equilibria for Reactive Extraction with TOA

The L/L equilibrium data for DMCCA in the system water—solvent with an extractant (TOA) are presented in Figs. 1 and 2. From Fig. 2 it can be seen that with increasing extractant concentration the value of the distribution coefficient increases. With increasing the concentration of the acid in the aqueous phase the distribution coefficient of DMCCA increases and at the acid concentration of about 0.02 kmol m^{-3} it approaches a maximum or at low TOA concentration a steady value.

An overloading of the extractant, amounting to values of loading of about 27 at the higher acid concentrations and of 7 at lower concentrations was ob-

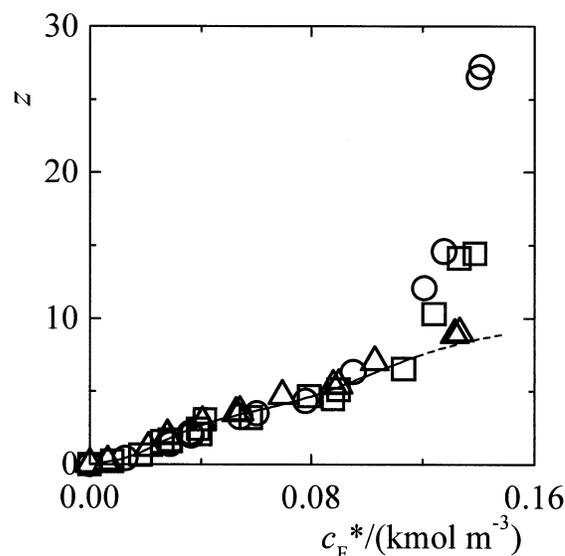


Fig. 4. Loading of the extractant TOA with DMCCA vs. equilibrium concentration of acid in the aqueous phase for different concentrations of the extractant in the solvents. Lines represent the correlation of experimental data with eqns (12, 13, 16, 23) considering mechanism I R and taking into account data with the concentration of acid in the aqueous phase below 0.12 kmol m^{-3} . The legend is the same as in Fig. 1.

served (Fig. 4). These values are higher than those observed for butyric acid where loadings up to 4.4 have been found [19, 26]. For lower acid concentrations, below about 0.12 kmol m^{-3} , the loading is independent of the extractant concentration, which suggests stoichiometry of the acid/extractant complexes ($p,1$), where p is the number of acid molecules per one molecule of extractant.

In modelling L/L equilibrium the formation of all possible complexes up to the value of $p = 14$ and the formation of a monomer and a dimer (mechanism I) or a trimer (mechanism II) were initially considered. The model was tested for experimental data with the concentration of acid in the aqueous phase below 0.12 kmol m^{-3} . The values of equilibrium constants for several complexes appeared to be negligibly small. When these constants were omitted and the number of complexes considered in the mechanism was reduced, the correlation coefficients and SSD did not change remarkably, as it is shown in Table 3 for mechanisms I R and II R. The reduced model II R, considering also the formation of the acid trimer, enables a slightly better fit to data with a lower value of SSD (Table 3). The reduced model I R with complexes (1,1), (3,1), (4,1), (6,1), and (10,1), together with a monomer and a dimer of acid, fits experimental data well, as shown in Figs. 1, 2, and 4. This model is suggested for modelling mass transfer in pertraction through liquid membranes or membrane-based solvent extraction.

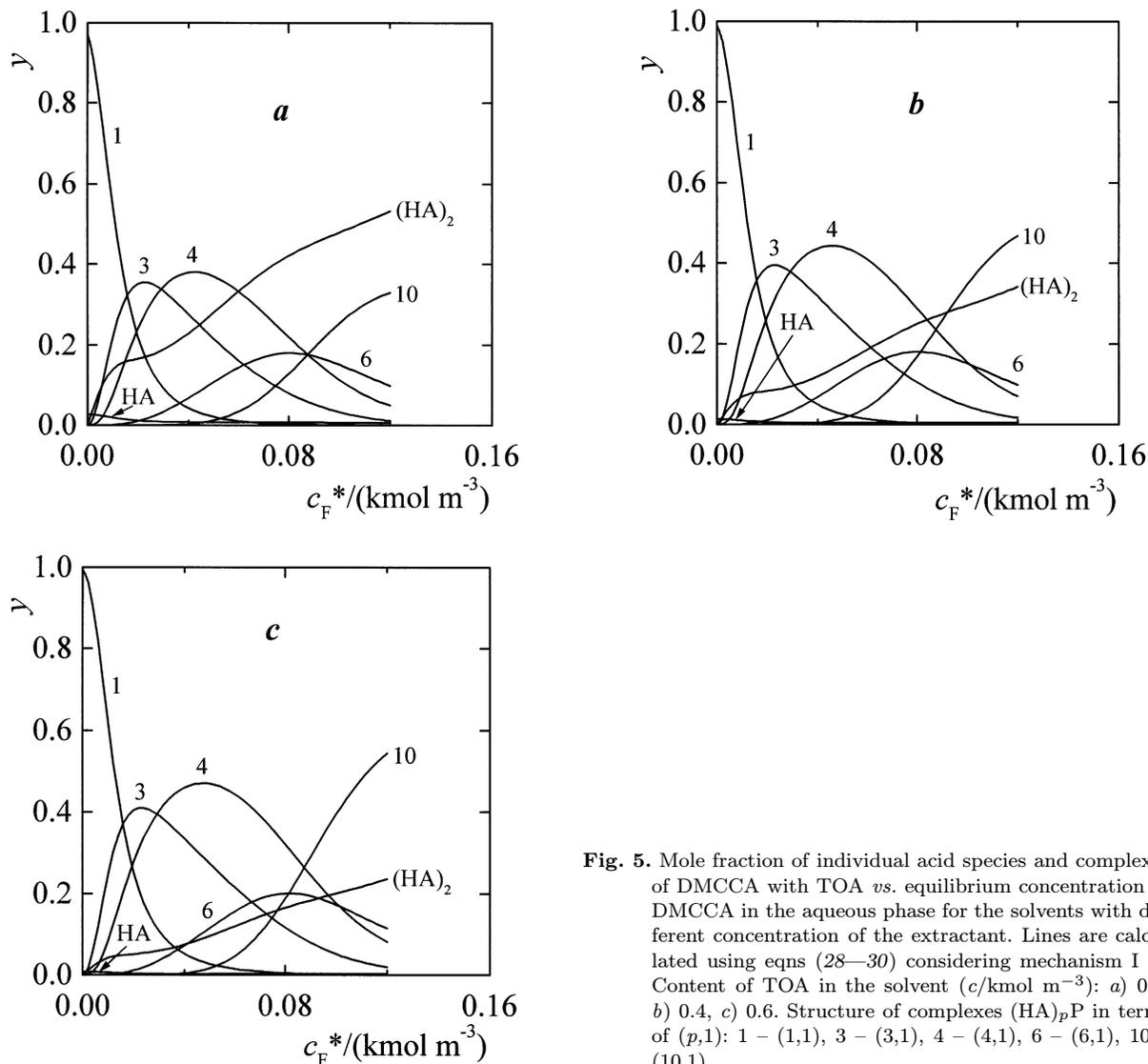


Fig. 5. Mole fraction of individual acid species and complexes of DMCCA with TOA vs. equilibrium concentration of DMCCA in the aqueous phase for the solvents with different concentration of the extractant. Lines are calculated using eqns (28–30) considering mechanism I R. Content of TOA in the solvent ($c/\text{kmol m}^{-3}$): a) 0.2, b) 0.4, c) 0.6. Structure of complexes $(\text{HA})_p\text{P}$ in terms of $(p,1)$: 1 – (1,1), 3 – (3,1), 4 – (4,1), 6 – (6,1), 10 – (10,1).

Fig. 5 reveals the distribution of species in terms of mole fractions of the monomer, dimer, and individual complexes in the solvent, defined by eqns (28–30). At low concentrations of acid, the most part of DMCCA in the solvent is in the form of the complex (1,1). Maxima on the dependences of mole fractions of the individual complexes of DMCCA are at the same values of the concentration of DMCCA for all concentrations of TOA tested. In the solvent with concentration 0.6 kmol m^{-3} of TOA the largest part of DMCCA is extracted by complexing with TOA. On the contrary, in the solvent with concentration 0.2 kmol m^{-3} of TOA, the physical extraction by alkanes is quite important and its share increases with the increasing concentration of DMCCA in the aqueous phase achieving the major part of extracted DMCCA (53 %). Thus, for the minimization of the unspecific (physical) interactions it would be preferable to use an organic solvent with concentrations of TOA higher than 0.2 kmol m^{-3} .

The mean number of acid molecules in the statis-

tical complex can be calculated by the relation

$$p_m = \sum_p p y_{p,1} \quad (34)$$

and it is shown in Fig. 6. The size of the mean complex (aggregate) increases rapidly up to the value of c_F^* of about 0.03 kmol m^{-3} and remains around of 3 up to $c_F^* = 0.06 \text{ kmol m}^{-3}$, and then it starts to increase sharply again. With increasing concentration of TOA the mean size of the complex increases.

Coextraction of Water

With increasing concentration of acid in the solvent, which is proportional to the acid concentration in the aqueous phase, also the water content in the solvent increases, as shown in Fig. 7. After subtraction of water dissolved in the pure solvent without DMCCA, the ratio of moles of water related to physical and reactive extraction of DMCCA to the overall

Table 3. Equilibrium Constants of the Mathematical Models Involving Different Chemistry of Extraction with Formation of Complexes of DMCCA with TOA of Different Structure

Structures of species considered in the model (<i>p</i> , <i>q</i>)	Mechanism			
	I	I R	II	II R
	$K_{p,q}/(\text{kmol m}^{-3})^{1-p-q}$			
(1,0)	0.1547	0.1547	0.1547	0.1547
(2,0)	2265	2265	1729	1729
(3,0)			2.397×10^4	2.397×10^4
(1,1)	25.12	25.12	26.44	26.44
(2,1)	2.140×10^{-12}		7.901×10^{-13}	
(3,1)	3.354×10^4	3.354×10^4	2.700×10^4	2.700×10^4
(4,1)	8.619×10^5	8.619×10^5	1.084×10^6	1.084×10^6
(5,1)	1.321×10^{-8}		1.912×10^6	1.912×10^6
(6,1)	5.613×10^7	5.613×10^7	1.716×10^{-8}	
(7,1)	1.133×10^{-6}		2.105×10^{-7}	
(8,1)	7.080×10^{-6}		1.675×10^{-6}	
(9,1)	3.761×10^{-5}		1.174×10^{11}	1.174×10^{11}
(10,1)	7.691×10^{11}	7.691×10^{11}	6.967×10^{-5}	
(11,1)	1.102×10^{-3}		4.211×10^{-4}	
(12,1)	6.589×10^{-3}		3.486×10^{-4}	
(13,1)	4.067×10^{-2}		1.509×10^{-2}	
(14,1)	2.498×10^{-1}		8.785×10^{-2}	
<i>r</i>	0.9953	0.9953	0.9957	0.9957
SSD	124.0	124.0	112.2	112.2
σ	1.230	1.167	1.170	1.111

p – number of DMCCA molecules, *q* – number of TOA molecules.

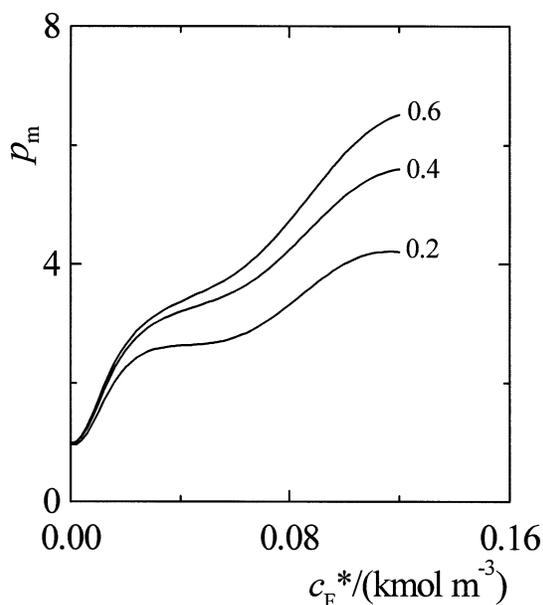


Fig. 6. Mean value of the number of acid molecules in the statistical aggregate vs. equilibrium concentration of DMCCA in the aqueous phase for the solvents with different concentration of the extractant. Lines are calculated using eqn (34) considering the mechanism I R. The numbers are the numerical values of concentrations of TOA in the solvent ($c/(\text{kmol m}^{-3})$).

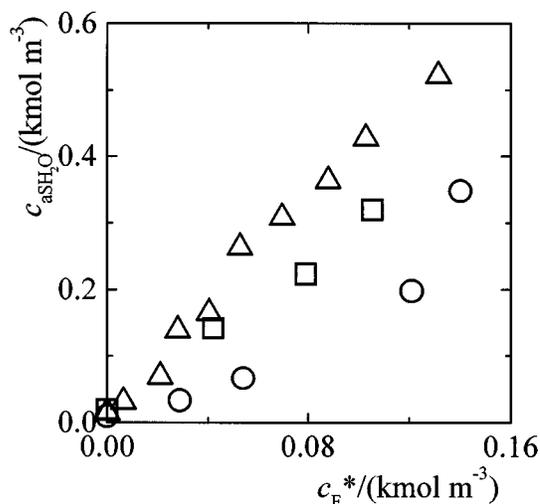


Fig. 7. Concentration of water in the solvent vs. equilibrium concentration of DMCCA in the aqueous phase. The legend is the same as in Fig. 1.

concentration of acid in the solvent is more or less independent of the acid concentration in the aqueous phase, as can be seen in Fig. 8.

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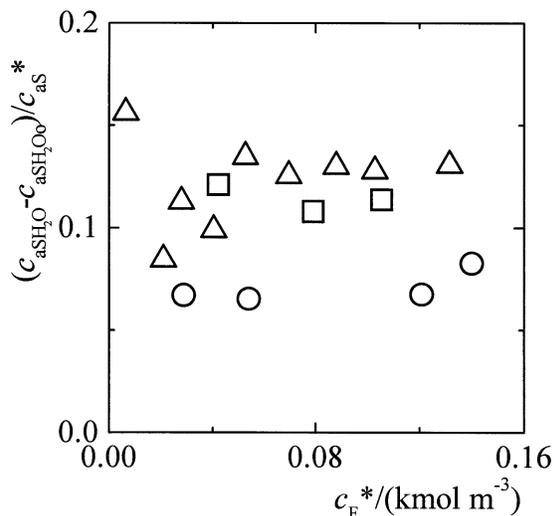


Fig. 8. Ratio of the change of water concentration, due to co-extraction in the solvent, to concentration c_{aS}^* vs. equilibrium concentration of DMCCA in the aqueous phase. The legend is the same as in Fig. 1.

SYMBOLS

$a(X)$	equilibrium activity of the species
B	quantity, defined by eqn (22)
c	molar concentration kmol m^{-3}
c_a	analytical (overall) molar concentration kmol m^{-3}
c_2	molar concentration of the acid dimer in the solvent kmol m^{-3}
c_3	molar concentration of the acid trimer in the solvent kmol m^{-3}
c_M	molar concentration of the acid monomer in the solvent kmol m^{-3}
c_P	molar concentration of the free extractant (TOA) in the solvent kmol m^{-3}
c_{P_0}	molar concentration of the extractant in the pure solvent (without acid) kmol m^{-3}
$c_{p,1}$	molar concentration of the $(p,1)$ complex in the solvent kmol m^{-3}
c_S	total molar concentration of the acid in the solvent kmol m^{-3}
D	distribution ratio, defined by eqn (6)
K_a	dissociation constant of DMCCA
K'_M	extraction constant of a monomer based on activities of species, defined by eqn (A)
K_M	extraction constant of a monomer based on molar concentrations of species, defined by eqn (1)
K'_p	equilibrium constant of formation of acid associates based on activities of species, defined by eqn (B)
K_2, K_3	equilibrium constants of formation of a dimer and trimer based on molar concentrations of species, defined by eqn (2) for $p = 2$ and 3 $(\text{kmol m}^{-3})^{1-p}$

$K_{p,1}$	equilibrium constant of formation of acid/extractant complexes with $(p,1)$ stoichiometry based on molar concentrations of species, defined by eqn (15) $(\text{kmol m}^{-3})^{-p}$
M	molar mass kg kmol^{-1}
n	amount of substance kmol
p_m	mean number of acid molecules in the statistical complex, defined by eqn (34)
r	correlation coefficient
SSD	sum of squares of differences of experimental and calculated data
V	volume m^3
V_{alk}	volume of alkanes (diluent) in the solvent with extractant and extracted acid m^3
V_{Aphys}	volume of acid physically extracted (dissolved) in the solvent with extractant m^3
X	quantity, defined by eqn (20)
Y	quantity, defined by eqn (10)
y	mole fraction of species, defined by eqns (28–30)
z	loading, defined by eqn (13)
φ	mass balance ratio, defined by eqn (33)
γ	kinematic viscosity
ρ	density kg m^{-3}
σ	relative standard deviation and correlation coefficients
[]	equilibrium molar concentration of the species shown in the brackets kmol m^{-3}

Indices

A	acid (DMCCA)
F	feed (aqueous phase)
M	monomer of acid
o	initial value
P	extractant (TOA)
p	quantity referring to the acid associate (dimer or trimer) in the organic phase with number of acid molecules in associate of p
p, q	quantity refers to the complex with (p, q) structure, where p is the number of the acid molecules coordinated or associated with q molecules of extractant (TOA)
$p, 1$	refers to the complex with $(p, 1)$ structure where p is the number of the acid molecules coordinated or associated with one molecule of extractant (TOA)
S	solvent (organic) phase
*	in equilibrium
overbar	shows the species in the solvent (organic) phase

Abbreviations

DMCCA	2,2-dimethylcyclopropanecarboxylic acid
HA	organic acid (DMCCA)

P extractant (TOA)
TOA trioctylamine

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